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(58) Field of search

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(54) Detergent composition

(57) A detergent composition useful to clean the hard surfaces is free from smelling like a solvent. It comprises

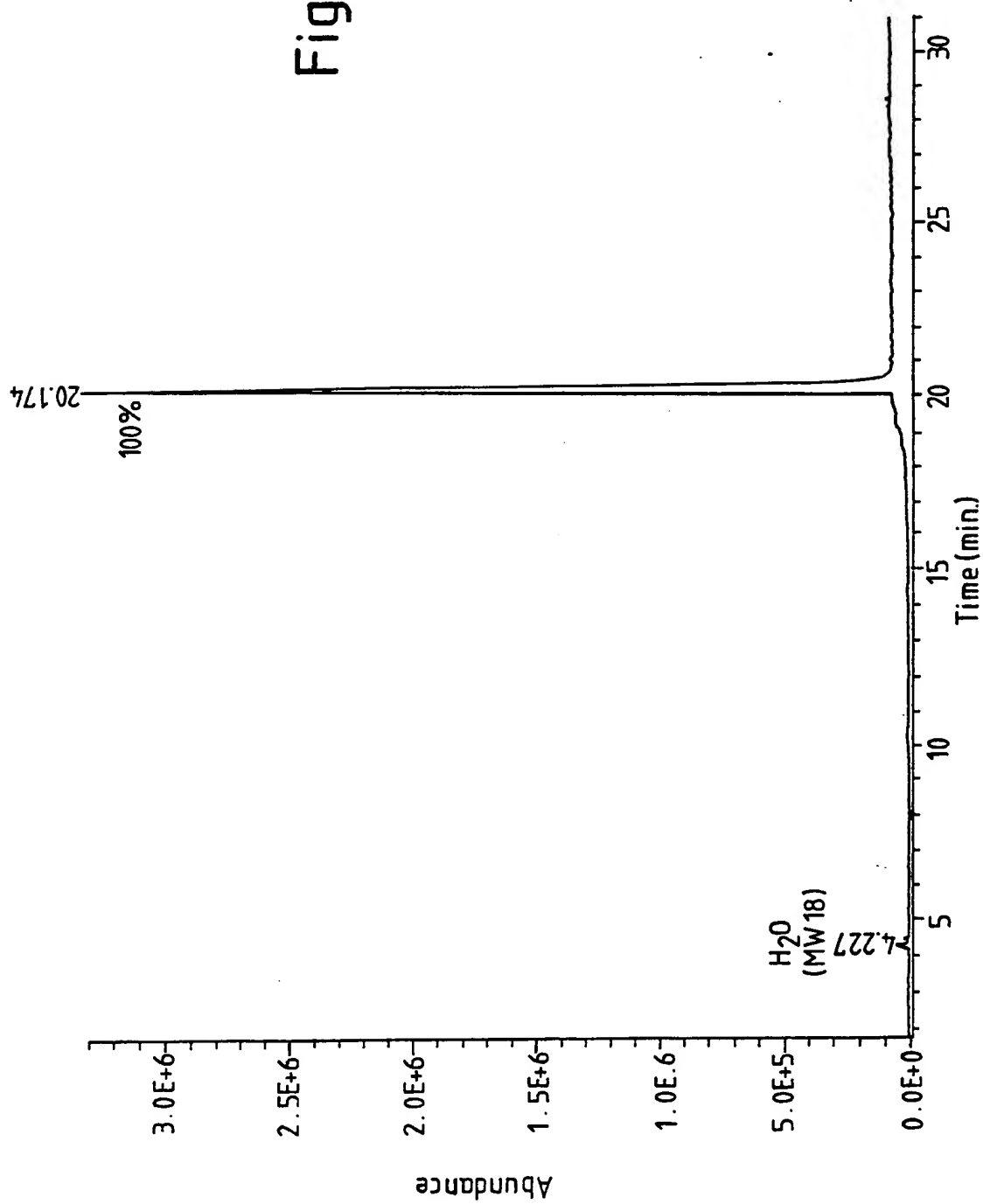
(A) 0.1 to 20% by weight of an alkylene glycol alkyl ether type solvent represented by the following general formula in which the content of a substance with a molecular weight of 50 to 300 other than the main ingredient in the solvent is such that the ratio of the peak area of the substance other than the main ingredient to the peak area of said solvent is less than 0.5% in a head space GC-MS analysis (measuring condition being defined in the specification):

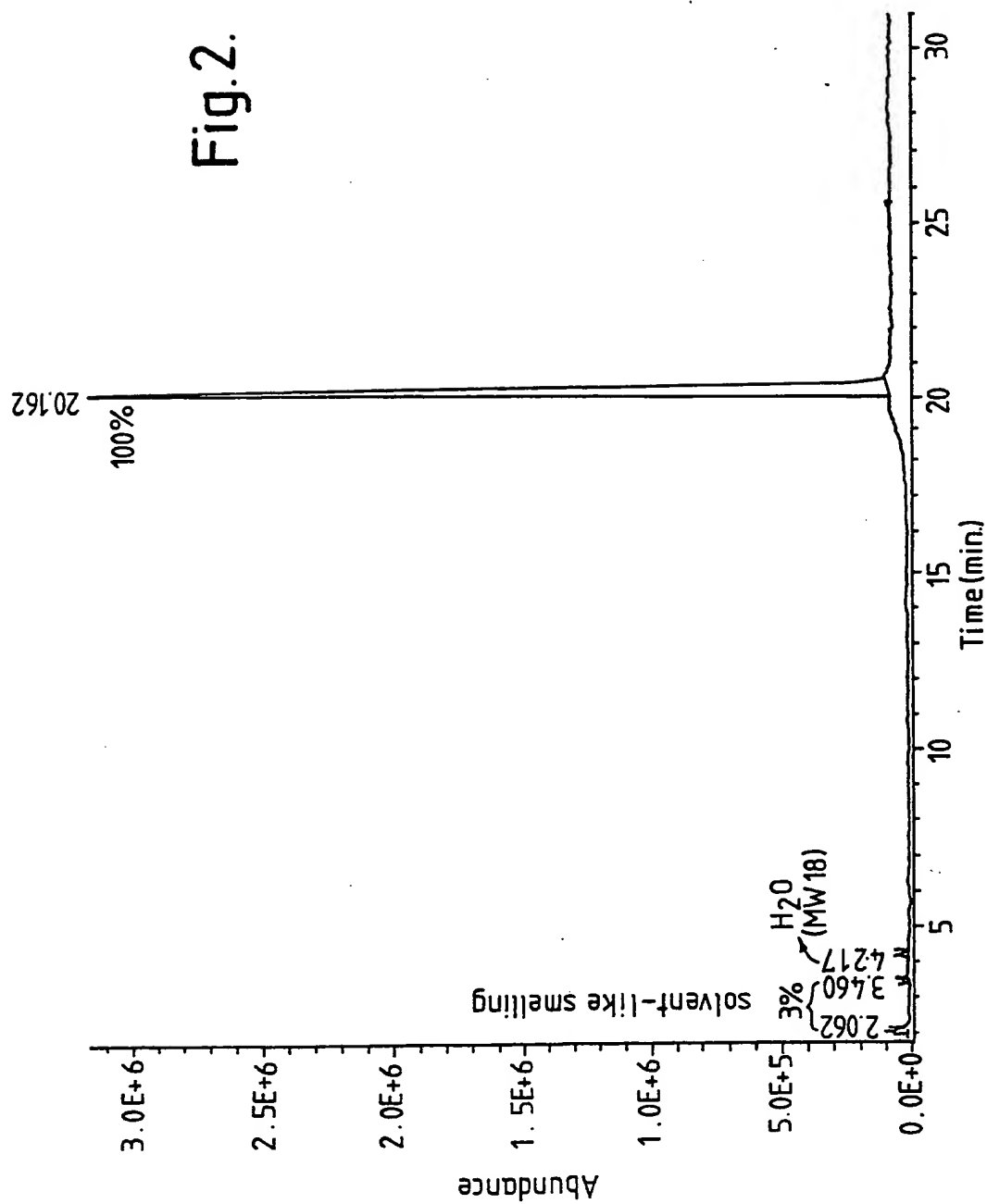


where R and R' each represents H or alkyl group with 1 to 8 carbon atoms providing that R and R' are not simultaneously H, X and Y each represents an integer:  $0 \leq X \leq 3$ ,  $0 \leq Y \leq 3$  providing that X and Y are not simultaneously 0, and

(B) 0.1 to 20% by weight of a surface active agent.

Fig.1.





## Detergent composition

### (Industrial Field of the Invention)

The present invention concerns a detergent composition and, more in particular, it relates to a liquid detergent composition for hard surface.

### (Prior Art)

Existent detergent compositions have been used selectively depending on the difference for the kinds and the degree of contaminations or stains. There has been mainly used surface active agent/solvent type detergents for thumb-mark contamination and not-modified oil contaminations of relatively moderate degree of contamination, surface active agent/solvent/alkali agent type detergents for oil and fat contamination, etc. denatured under the effect of heat, sunlight and oxygen in air (in kitchen or the like) and surface active agent/solvent/metal chelating type detergents for metal soap, in particular, calcium salt of fatty

acid in bath rooms.

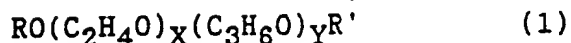
Further, for the solvent as the main ingredient of the detergent, alkylene glycol alkyl ether type solvents prepared by adding ethylene oxide and/or propylene oxide to a lower alcohol are generally used in view of damages to substrates. Although various detergents which are satisfactory to some extent for the level of detergent power have been proposed by using such solvents (Japanese Patent Publication Sho 50-40126, Japanese Patent Laid-Open Sho 54-158408, 61-151300, Japanese Patent Publication Sho 55-9036 and Japanese Patent Laid-Open Hei 1-221497). On the other hand, since they release odors inherent to solvents, they give unpleasant feeling upon use, require masking by the addition of perfume ingredient or the like and have not yet reached a satisfactory level in view of odors even with addition of the perfume ingredient.

Further, although it has been proposed in Japanese Patent Laid-Open Hei 2-132199 to improve an odor by restricting the isomer content in a specific solvent (propylene oxide adduct of a lower alcohol), the solvent odor can not yet been eliminated completely.

( Summary of the Invention )

The present inventors have made an analysis for the fundamental cause of the solvent odor in the alkylene glycol alkyl ether type solvent represented by the following general

formula (1) used in the detergent composition:



where R and R' each represents H or alkyl group with 1 to 8 carbon atoms providing that R and R' are not simultaneously H, X, Y each represents an integer:  $0 \leq X \leq 3$ ,  $0 \leq Y \leq 3$  providing that X and Y are not simultaneously 0 and, further, made studies on the solvent with no solvent odor and, as a result, it has been found that the cause for the unpleasant solvent odor is not an odor possessed by the solvent itself represented by the general formula (1), but it is attributable to a slight amount of volatile substance which is by-produced upon production or derived from raw material.

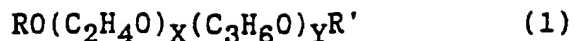
Further, as a result of the measurement for the solvent by a head space analysis (conditions are to be described later), it has been found that those having the solvent odor contain, in addition to the compound represented by the general formula (1) as the main ingredient, by-products having a molecular weight of 50 to 300 by 1 to 3%, more particularly, 4 to 20% based on the peak area of the compound represented by the general formula (1).

In view of the above, when solvent specimens of different content of by-products were obtained by varying the reaction conditions and analysis for the head space in

such specimens and evaluation for the odor were conducted. As a result, it has been found that a solvent with the content of the molecular weight of 50 to 300 in the head space of less than 0.5% relative to the peak area of the main ingredient is at a level free from the problem in view of the odor.

In view of the foregoing results, the present inventors et al have accomplished the present invention based on the finding that an extremely excellent detergent composition can be provided in view of the odor as well as the detergent power, by blending a slight amount of by-product with 50 to 300 molecular weight contained in those considered to have a solvent odor with a solvent free from solvent odor, obtained by reducing the peak area ratio by the GC-MS analysis in the head space to less than 0.5%.

That is, the present invention provides a detergent composition comprising: (A) 0.1 to 20 % by weight of an alkylene glycol alkyl ether type solvent represented by the following general formula in which the content of a substance with a molecular weight of 50 to 300 other than the main ingredient in the solvent is such that the ratio of the peak area of the substance other than the main ingredient to the peak area of said solvent is less than 0.5% in a head space GS-MS analysis (measuring condition being defined in the specification):



where R and R' each represents H or alkyl group with 1 to 8 carbon atoms providing that R and R' are not simultaneously H, X, Y each represents an integer:  $0 \leq X \leq 3$ ,  $0 \leq Y \leq 3$  providing that X and Y are not simultaneously 0, and

(B) 0.1 to 20 % by weight of a surface active agent.

In the present invention, the head space GM-MS analysis for the compound represented by the general formula (1) in the present invention is carried out as below.

(1) Measuring Instrument

Head space sampler

HP 19395 A

manufactured by Hewlett Packard Co



Gas chromatography

HP 5890 SERIES II



Detector HP 5971 A

MASS SELECTIVE DETECTOR

MASS range 10 - 400

(2) Conditions for Gas chromatography

Column --- manufactured by J and W Co. DB-WAX



30m x 0.32 x 50 um

Carrier gas -- He, 1.84 ml/min

Split vent. 20.0 ml/min

Total Split vent. 125 ml/min

Column temperature elevation condition

Time

0 - 2 min --- constant at 40°C

2 - 12 min --- elevated up to 80°C at a rate of  
4°C/min

12 - 19 min --- elevated up to 150°C at a rate of  
10°C min

19 - 31 min --- constant at 150°C

Specimen charging temperature 230°C

Detector temperature 250°C

(3) Conditions for head space

Sample vessel -- 20 ml vial vessel

Sample amount -- 10 ml

Heating condition -- 90°C x 1.5 hr

As the solvent (A) usable in the present invention, there can be mentioned, for example, ethylene glycol monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monobutyl ether, tripropylene glycol dimethyl ether, polyoxyethylene (X = 1 in the formula (1)) polyoxypropylene (Y = 3 in the formula (1)) glycol monobutyl ether, etc. It is necessary for the content of the by-

product in such a solvent that the ratio of the peak area for the by-product other than the main ingredient based on the peak area of the solvent is less than 0.5% by weight. If the peak area ratio exceeds 0.5%, a detergent composition which is satisfactory in view of the odor can not be obtained. The solvent (A) is blended in the composition according to the present invention by from 0.1 to 20% by weight, preferably, 3 to 10% by weight.

As the surface active agent (B) used in the present invention, an anionic surface active agent and nonionic surface active agent are preferred but an amphoteric surface active agent and a cationic surface active agent can also be used as required.

As the anionic surface active agent, usual sulfonate type anionic surface active agent and sulfate type anionic surface active agent are used. As the sulfonate type anionic surface active agent, there can be mentioned linear or branched alkyl ( $C_8 - C_{22}$ ) benzene sulfonate, long-chained alkyl ( $C_8 - C_{22}$ ) sulfonate and long-chained olefin ( $C_8 - C_{22}$ ) sulfonate. Further, as the sulfate type anionic surface active agent, there can be mentioned, for example, long-chained monoalkyl ( $C_8 - C_{22}$ ) sulfate ester salt, polyoxyethylene (1 - 6 mol) long-chained alkyl ( $C_8 - C_{22}$ ) ether sulfate ester and polyoxyethylene (1 - 6 mol) alkyl ( $C_8 - C_{22}$ ) phenyl ether sulfate ester salt. Cations as

pair ions in such anionic surface active agents are, for example, alkali metal ion such as of sodium and potassium and alkanol amine ions such as of monoethanolamine, diethanolamine and triethanolamine. As the anionic surface active agent in the present invention, a sulfonate type surface active agent is preferred in view of the high resistance to hydrolysis, etc. Further, in view of the detergent power or the like, a linear or branched alkyl benzene sulfonate is preferred.

As the nonionic surface active agent, there can be used, for example, polyethylene (6 - 35 mol) long-chained alkyl (primary or secondary  $C_8 - C_{22}$ ) ether, polyoxyethylene (6 - 35 mol) alkyl ( $C_8 - C_{18}$ ) phenyl ether and polyoxyethylene polyoxypropylene block copolymer. In view of the detergent power or the like, polyoxyethylene (6 - 35 mol) long-chained alkyl (primary or secondary  $C_8 - C_{22}$ ) ether and polyoxyethylene (6 - 35 mol) alkyl ( $C_8 - C_{18}$ ) phenyl ether.

As the amphoteric surface active agent, there can be mentioned, for example, carbobetaine, sulfobetaine or hydroxy-sulfoxybetaine containing alkyl group with 8 to 22 carbon atoms.

Further, as the cationic surface active agent, there can be mentioned  $C_{10} - C_{22}$  mono-long-chained alkyl trimethyl ammonium salt, di-long-chained alkyldimethyl

ammonium salt and mono-long-chained alkyldimethyl benzyl ammonium salt.

Such a surface active agent (B) is blended by from 0.1 to 20% by weight in the composition according to the present invention.

An antioxidant may further be added to the detergent composition according to the present invention to prevent aging degradation of odor. As the antioxidant (C) used in the present invention, any of those known so far can be used and there can be preferably mentioned phenolic antioxidant such as 3,5-di-tert-butyl-4-hydroxytoluene and 2,5-di-tert-butylhydroquinone; amine type antioxidant such as N,N'-diphenyl-p-phenylenediamine and phenyl-4-piperidinyl carbonate; sulfur type antioxidant such as didodecyl-3,3'-thiodipropionate, and ditridecyl-3,3'-thiodi propionate, phosphoric antioxidant such as tris(isodecyl)phosphite and triphenyl phosphite; a natural antioxidant such as L-ascorbic acid and its sodium salt and DL- $\alpha$ -tocopherol, which may be used alone or as a combination of one or more of them. Among them, 3,5-di-tert-butyl-4-hydroxytoluene, 2,5-di-tert-butylhydroquinone and DL- $\alpha$ -tocopherol are particularly preferred. Such an antioxidant is blended to the solvent (A) in the detergent composition according to the present invention at a ratio of greater than 0.005 % by weight, preferably, from 0.005 to 5% by weight and,

more preferably, from 0.01 to 0.3% by weight. The anti-oxidant may be added during preparation of the solvent (A) or upon conditioning the detergent composition according to the present invention.

To the detergent composition according to the present invention, there may be blended an alkali agent such as monoethanolamine or diethanolamine, citric acid or metal ion chelating agent such as EDTA depending on the purpose of use, or optionally blended a low temperature stabilizer such as lower alcohol for example, ethanol, ethylene glycol, benzene sulfonate and toluene sulfonate, perfume, dye, corrosion inhibitor and/or antiseptic.

#### Brief Explanation of the Drawings

Fig. 1 is a chart for the head space GC-MS analysis for butyl carbitol according to the present invention and Fig. 2 is a chart for the head space GC-MS analysis for butyl carbitol in for comparison.

(Example)

The present invention will now be explained referring to examples but the invention is restricted only to the examples.

Examples 1 - 5 and Comparative Examples 1 - 5

Various kinds of detergent compositions of ingredient compositions shown in Table 1 were prepared, the odor for each of which was evaluated by 20 panelers and average values for the scores were determined.

The standards for the evaluation are as shown below.

- 4 ... no unpleasant odor
- 3 ... no substantial unpleasant odor
- 2 ... some unpleasant odor
- 1 ... unpleasant odor

Charts of the head space GC-MS analysis for butyl carbitol used in the examples and the comparative examples are shown in Fig. 1 and Fig. 2, respectively.

Examples 6 - 9 and Comparative Examples 6 - 9

Various kinds of detergent compositions of the ingredient compositions shown in Table 2 were prepared and odors of specimens just after the preparation and after one month storage at 50° C were evaluated by ten panelers and average values for the scores were determined.

The standards for the evaluation are as shown below.

- 4 ... no unpleasant odor
- 3 ... no substantial unpleasant odor
- 2 ... some unpleasant odor
- 1 ... unpleasant odor

Table 1

	Example					Comparative Example				
	1	2	3	4	5	1	2	3	4	5
Polyoxyethylene ( $\bar{p}=7$ ) alkyl ( $\bar{c}=12$ ) ether	3					3				
Sodium alkyl ( $\bar{c}=12$ ) benzene sulfonate		3	3	3			3	3		
N,N-dodecyltrimethyl-N-sulfo propyl ammonium betaine									5	
Dodecyltrimethyl ammonium chloride					3					5
Butyl carbitol (peak area ratio: less than 0.1%)	10	10	10	10	10					
Butyl carbitol (peak area ratio 3%)						10	5	5	5	5
Monoethanolamine		5					5			
Sodium ethylenediamine tetraacetate			5					5		
Water	balance	balance	balance	balance	balance	balance	balance	balance	balance	balance
pH	7.0	10.8	7.0	7.0	7.0	7.0	10.8	7.0	7.0	7.0
Score for odor	4.0	3.9	4.0	4.0	3.9	1.1	1.2	1.3	1.3	1.3

(1) Balancing amount for making the entire amount to 100

(2) pH was adjusted with NaOH or HCl

Table 2

	Example				Comparative Example				
	6	7	8	9	6	7	8	9	
Polyoxyethylene ( $\bar{p}=12$ ) alkyl ( $\bar{c}=12$ ) ether	5	5	5	5	2	2	2	—	
Sodium alkyl ( $\bar{c}=12$ ) benzene sulfonate	—	—	—	—	3	3	—	2	
Polyoxyethylene ( $\bar{p}=3$ ) alkyl ( $\bar{c}=12$ ) ether sulfonate ester sodium salt	—	—	—	—	—	—	3	2	
Butyl carbitol (peak area ratio: less than 0.1%)	5	5	5	5	—	—	—	—	
Butyl carbitol (peak area ratio: 3%)	—	—	—	—	5	5	5	5	
3,5-di-tert-butyl-4-hydroxytoluene	—	0.05	—	—	—	0.05	—	—	
DL- $\alpha$ -tocopherol	—	—	0.05	—	—	—	0.05	—	
2,5-di-tert-butylhydroquinone	—	—	—	0.05	—	—	—	0.05	
Monoethanolamine	—	—	5	—	—	—	3	—	
Sodium ethylenediamine tetraacetate	—	—	—	5	—	—	—	3	
Water 1)	balance	balance	balance	balance	balance	balance	balance	balance	
pH 2)	7.0	7.0	10.8	7.0	7.0	7.0	10.8	7.0	
Score for odor just after preparation	4.0	4.0	4.0	4.0	1.5	1.4	1.5	1.5	
Score for odor after one month storage at 50°C	3.3	3.9	3.9	3.9	1.0	1.1	1.1	1.0	

(1) Balancing amount for making the entire amount to 100

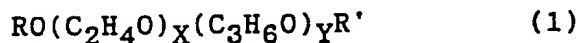
(2) pH was adjusted with NaOH or HCl



What is Claimed is

(1) A detergent composition comprising:

(A) 0.1 to 20 % by weight of an alkylene glycol alkyl ether type solvent represented by the following general formula in which the content of a substance with a molecular weight of 50 to 300 other than the main ingredient in the solvent is such that the ratio of the peak area of the substance other than the main ingredient to the peak area of said solvent is less than 0.5% in a head space GS-MS analysis (measuring condition being defined in the specification):



where R and R' each represents H or alkyl group with 1 to 8 carbon atoms providing that R and R' are not simultaneously H, X, Y each represents an integer:

$0 \leq X \leq 3$ ,  $0 \leq Y \leq 3$  providing that X and Y are not simultaneously 0, and

(B) 0.1 to 20 % by weight of a surface active agent.

(2) A detergent composition as defined in claim 1 which further contains an antioxidant by more than 0.005 % by weight based on the ingredient (A).

(3) A detergent composition as defined in claim 2, wherein the antioxidant is selected from the group consisting of 3,5-di-tert-butyl-4-hydroxytoluene, DL- $\alpha$ -tocopherol and 2,5-di-tert-butylhydroquinone.